PRODUCTION OF BIODIESEL FROM RUBBER SEED

KARTHIK A/L VASUTHEAVAN

Thesis submitted in partial fulfillment of the requirements
for the award of the degree of
Bachelor of Chemical Engineering

Faculty of Chemical and Natural Resources Engineering
UNIVERSITI MALAYSIA PAHANG

JANUARY 2012

ABSTRACT

The objective of this research is to produce biodiesel from rubber seed oil. Rubber seed oil (RSO) was obtained from rubber seed by soxhlet and microwave assisted extraction methods. Hexane was used as a solvent in the soxhlet extraction process. The yield of oil from rubber seed by soxhlet extraction method was found to be higher (34 – 40%) than by the microwave extraction method (30 – 32%). The physic-chemical properties of the RSO was measured and it was found that the RSO contained 22 wt.% of free fatty acids (FFA). The viscosity of the oil was found as 33.2 cm^2/s at 40^oC. Biodiesel was prepared by two-step method, where in the first step, the FFA was converted to fatty acid ethyl ester (FAEE) by acid catalyzed esterification, and in the second step the triglycerides (TG) was converted to FAEE by base catalyzed transesterification. Effect of different parameters, such as ethanol/oil molar ratio, temperature, catalyst concentration had been studied for both steps. In the first step, which is acid catalyzed esterification, the optimum parameters were found as 1:6 molar ratio of oil to ethanol, 0.5% of catalyst (H2SO4) and at 50^oC. The product from the first step was separated in a separating funnel to draw off the excess alcohol, catalyst and water. The optimum parameters for the second step were as follows: 1:6 molar ratio of oil to ethanol, 0.5wt.% of catalyst (NaOH) and temperature of 50^oC. After gravity separation of biodiesel from the glycerene layer, it was washed with hot water until a translucent product was obtained. The biodiesel was dried in the rotary vacuum evaporator at 100C for 1 h and the product was characterized. The viscosity of the final biodiesel was found as 5.92 cm^2/s and FFA content was undetectable. The gas chromatography analysis shows that the amount of methyl ester found in the sample is quite high.

ABSTRAK

Objektif kajian ini adalah untuk menghasilkan biodiesel dari minyak biji getah. Minyak biji getah (RSO) telah diperolehi daripada benih getah oleh kaedah gelombang mikro soxhletand pengekstrakan dibantu. Heksana telah digunakan sebagai asolvent dalam proses soxhletextraction. Hasil minyak dari biji getah melalui kaedah pengekstrakan soxhlet adalah didapati lebih tinggi (34 - 40%) berbanding dengan kaedah pengekstrakan gelombang mikro (30 - 32%). Ciri-ciri kimia obat urus-RSO itu adalah diukur dan didapati bahawa RSO mengandungi 22 berat.% Daripada asid lemak bebas (FFA). Kelikatan minyak yang ditemui sebagai 33.2 cm^2 / s pada 40^oC. Biodiesel telah disediakan oleh kaedah dua langkah, di mana dalam langkah pertama, FFA telah ditukar kepada asid lemak etil ester (FAEE) oleh esterification catalyzed asid, dan dalam Langkah kedua trigliserida (TG) telah ditukar kepada FAEE oleh transesterification catalyzed asas. Kesan parameter yang berbeza, seperti etanol / nisbah minyak molar, suhu, kepekatan pemangkin telah dikaji bagi kedua-dua langkah-langkah. Dalam langkah pertama, yang esterification catalyzed asid, parameter optimum telah didapati sebagai 1:06 nisbah molar minyak etanol, 0.5% daripada pemangkin (H_2SO_4) dan pada 50^oC. Produk dari langkah yang pertama telah dipisahkan dalam saluran memisahkan menarik alkohol yang berlebihan, pemangkin dan air. Parameter optimum untuk langkah kedua adalah seperti berikut: 1:06 molar nisbah minyak etanol, 0.5wt% pemangkin (NaOH) dan suhu 50^oC.. Selepas pemisahan graviti biodiesel dari lapisan glycerene, ia telah dibasuh dengan air panas sehingga produk lut telah diperolehi. Biodiesel ini dikeringkan di dalam penyejat vakum putar pada 100C selama 1 h dan produk dicirikan. Kelikatan biodiesel akhir ditemui sebagai 5,92 cm^2 / s dan kandungan FFA tidak dapat dikesan. Analisis gas kromatografi menunjukkan bahawa jumlah methyl ester yang terdapat di dalam sampel adalah agak tinggi.

TABLE OF CONTENTS

4 RESULT AND DISCUSSION

LIST OF TABLES

LIST OF FIGURES

LIST OF SYMBOLS

P	-	Pressure
m	-	Mass
^{o}C	-	Degree Celsius
kg	-	Kilogram
K	-	Degree Kelvin
mL	-	Mililiter

LIST OF APPENDICE

CHAPTER 1

INTRODUCTION

1.1 Overview of research

Many years before the first diesel engine become functional, scientists E.Duffy and J.Patrick has conducted the transesterification of a vegetable oil as early as 1853. After that, on 10 August of 1893, Rudolf Diesel's prime model that is an engine ran on its own power by only using peanut oil as the fuel. That is the day that called "International Biodiesel Day". In 1912, Rudolf Diesel had said that the use of vegetable oils for engine fuels may seem insignificant during his time but it may become as important as petroleum and the coal-tar products in future. Just like he said, now the non edible oil from vegetable oils is more attractive then edible oils in this present time. The non edible oil from vegetable oils and animal fats is used in many applications. One of the applications is production of biodiesel.

Biodiesel is a renewable source. Biodiesel refers to a vegetable oil or animal fats based diesel fuel consisting of long chain alkyl esters such as methyl, propyl or ethyl. Biodiesel is produced by chemically reacting vegetable oil such as rubber seed oil (RSO) with an alcohol such as methanol. At the present time, biodiesel is being preferred more than the petroleum fuel because of the high oil prices and to limit greenhouse gas emissions. Biodiesel is also safe, non-toxic and biodegradable in water, contains less sulfur and has a high flash point (>130c). Biodiesel is also less polluting than petroleum diesel because combustion of biodiesel produces less carbon monoxide, unburned hydrocarbons and sulfur dioxide.The lubricating effects of the biodiesel also may extend the lifetime of engines.

Vegetable oils have high viscosity and hence four methods used to reduce the high viscosity of the oil. The four methods are dilution, micro emulsion, pyrolysis and transesterification. But, in the present time biodiesel is mainly produced by the transesterification process of vegetable oils or animal fats and also by the extraction from algae. Transesterification is the reaction of a animal fat or vegetable oil with an alcohol to form esters and glycerol. Glycerol is used in many common products such as soap; hence there is a little waste that should be cleared in that product.

Rubber seeds or also known as *Heveabrasiliensis,* are an abundant source of non edible oil that is available in Malaysia. The seeds also remain underutilized although the oil produced can be used in many applications. Mechanical extraction process used to extract the oil from rubber seeds. Rubber seed oil (RSO) contains high in free fatty acids (FFA) that makes the oil feasible to use in the production of biodiesel. According to its free fatty acid composition, rubber seed oil is rich in unsaturated fatty acid such as oleic acid linoleic acid and linolenic acid. Hence, rubber seed oil is a good source for the production of biodiesel.

There are many type of transesterification process. Example of it is;

1. Homogeneous alkali (base) catalyzed transesterification
2. Homogeneous acid-catalyzed transesterification
3. Two step method esterification.

The Transesterification process is the reaction of a triglyceride (fat/oil) with an alcohol to form esters and glycerol. A triglyceride has a glycerine molecule as its base with three long chain fatty acids attached. The characteristics of the fat are determined by the nature of the fatty acids attached to the glycerine. The nature of the fatty acids can in turn affect the characteristics of the biodiesel. During the esterification process, the triglyceride is reacted with alcohol in the presence of a catalyst, usually a strong alkaline like sodium hydroxide. The alcohol reacts with the fatty acids to form the mono-alkyl ester, or biodiesel and crude glycerol. In most production methanol or ethanol is the alcohol used (methanol produces methyl esters, ethanol produces ethyl esters) and is base catalysed by either potassium or sodium hydroxide. Potassium hydroxide has been found to be more suitable for the ethyl ester biodiesel production, either base can be used for the methyl ester. A common product of the transesterification process is Rape Methyl Ester (RME) produced from raw rapeseed oil reacted with methanol.

Successful transesterification reaction is signified by the separation of the ester and glycerol layers after the reaction time. The heavier, co-product, glycerol settles out and may be sold as it is or it may be purified for use in other industries, e.g. the pharmaceutical, cosmetics etc.

Straight vegetable oil (SVO) can be used directly as a fossil diesel substitute however using this fuel can lead to some fairly serious engine problems. Due to its relatively high viscosity SVO leads to poor atomisation of the fuel, incomplete combustion, coking of the fuel injectors, ring carbonisation, and accumulation of fuel in the lubricating oil. The best method for solving these problems is the transesterification of the oil.

The engine combustion benefits of the transesterification of the oil are:

- Lowered viscosity
- Complete removal of the glycerides
- Lowered boiling point
- Lowered flash point
- Lowered pour point

Biodiesel is a clean burning alternative fuel, produced from domestically grown, renewable resources. Biodiesel contains no petroleum products, but can be blended at any concentration with diesel from fossil sources to create a biodiesel blend. It can be used in compression-ignition (diesel) engines with little or no modification. Biodiesel is simple to use, biodegradable, non-toxic, and basically free of sulphur compounds and aromatics.

When Rudolf Diesel designed his prototype diesel engine a century ago, he ran it on peanut oil. He planned that diesel engines would operate on a variety of vegetable oils. But when petroleum diesel fuel arrived on the marketplace, it was cheap, reasonably efficient, and readily available, and therefore quickly became the diesel fuel of choice.

Biodiesel is made in a chemical process called transesterification, where organically derived oils (vegetable oils, animal fats and recycled restaurant greases) are combined with alcohol (usually methanol) and chemically altered to form fatty esters such as methyl ester. The biomass-derived esters can be blended with conventional diesel fuel or used as a neat fuel (100% biodiesel). The process results in two products -- methyl esters (the chemical name for biodiesel) and glycerine (a valuable by-product usually sold for use in the production of soap).

Biodiesel should not be confused with straight vegetable oil! Fuel-grade biodiesel is produced to strict industry specifications (ASTM D6751 in the US) in order to ensure proper combustion and engine performance. Biodiesel is the only alternative fuel for motor vehicles up to now (2004) to have fully completed the health effects testing requirements of the 1990 Clean Air Act Amendments. Biodiesel that meets ASTM D6751 and is registered with the Environmental Protection Agency is a legal motor fuel for sale and distribution as such. Raw vegetable oil cannot meet biodiesel fuel specifications, it is not registered with the EPA, and it is not a legal motor fuel, despite widespread use in many areas. To express it more exactly: Biodiesel is defined as mono-alkyl esters of long-chain fatty acids derived from vegetable oils or animal fats, conforming to ASTM D6751 specifications for use in diesel engines. Biodiesel refers to the pure fuel before blending with diesel fuel.

Biodiesel is less damaging to the environment because it is made from renewable resources and has lower emissions compared to fossil diesel. The toxic effects are even less than from table salt and it biodegrades as fast as sugar when spilled. Since it is made from renewable resources such as rape seeds or similar oil plants, its use decreases dependence on imported oil, whilst contributing to the local rural economy.

With agricultural commodity prices approaching record lows, and petroleum prices reaching ever new record highs, it is clear that more can be done to utilize domestic surpluses of vegetable oils while enhancing energy security. Oil plants will grow in many areas where other agriculture is possible. Because biodiesel can be manufactured using existing industrial production capacity, and is used with conventional equipment, it provides a very good way of securing energy supplies in the short term.

Increased utilization of renewable biofuels can result in measurable micro-economic benefits for both the industrial and agricultural sectors as well as positively affecting the balance of trade. A study completed in 2001 by the U.S. Department of Agriculture states that an annual increase by the equivalent of 760 million litres of soy-based biodiesel demand would boost the total cash receipts from crops by USD5.2 billion cumulatively by 2010, leading to an average farm income increase of USD300 million per year net over this period. In addition to being a domestically produced, renewable alternative fuel for diesel engines, biodiesel has positive performance attributes such as increased cetane number, high fuel lubricating value and high oxygen content.

Biodiesel is one of the most rigorously tested alternative fuels on the market. A number of independent studies have been completed with the results showing biodiesel performs as well as fossil diesel whilst causing much less damage to the environment and human health compared to diesel. That research includes studies performed by the U.S. Department of Agriculture, U.S. Department of Energy, Stanadyne Automotive Corp., Lovelace Respiratory Research Institute, and Southwest Research Institute. Biodiesel is the first and, up to now, the only alternative fuel to have completed the rigorous Health Effects testing requirements of the Clean Air Act. Biodiesel has been shown to perform similarly to diesel in more than 80 million successful road kilometres, using virtually all types of diesel engines, a great deal of off-road distance and countless marine hours. There are now more than 300 major fleets use the fuel in the US alone.

Pure biodiesel (B100) has a solvent effect, which may well release deposits accumulated on tank walls and in pipes from operation. It will also attack paint and similar surfaces, given the chance. Using high blends of biodiesel, the release of deposits may clog filters initially and care should be taken to replace fuel filters until the build-up of deposits is eliminated. This issue is less of a problem with B20 blends, and there is no evidence that lower-blend levels such as B2 have caused filters to become blocked.

B20 and B2 refer to the American system of designating the percentage of biodiesel in a blend. B20 contains 20 % biodiesel and B2 contains 2 % biodiesel by volume. The rest will consist of standard fossil diesel fuel.

The recent switch to low-sulphur diesel fuel has caused most OEMs to switch to components that are also suitable for use with biodiesel. In general, biodiesel used in pure form can soften and degrade certain types of elastomers and natural rubber compounds relatively quickly. These were commonly used in engines up to a few years ago, so there may be a compatibility issue with older vehicles. Using high percentage blends can impact fuel system components (primarily fuel hoses and fuel pump seals) that contain elastomer compounds incompatible with biodiesel, although the effect is lessened as the biodiesel blend level is decreased. Experience has shown that no changes to gaskets or hoses are necessary when using B20, even in older engines.

The final issue to be covered is that of shelf life. Most fuel today is used up long before six months, and many petroleum companies do not recommend storing hydrocarbon diesel for more than ix months. The current industry recommendation is that biodiesel be used within six months, or reanalysed after six months to ensure the fuel meets ASTM specifications (D-6751).

On the negative side, biodiesel does not supply the same energy yield per area that energy plants for use in a biodigester would. The methane produced there would give about twice the energy that the same area devoted to oil plants for biodiesel production would recover. Biodiesel has the great advantage of being useable in existing engines with very little being needed in the way of adaptation. In cold climates it will probably prove impossible to use pure biodiesel (B100), but mixtures up to 20 % biodiesel (B20) should cope with most climates. Preheating of the fuel is also a possibility, which is unavoidable in many areas, even using standard diesel from fossil sources. This advantage means that the technology can be applied generally without any preparation stage. Converting fleets of vehicles to gas propulsion is a very costly and time-consuming business, to say nothing of the down-time caused.

Biodiesel, generally in the form of B20, is used in federal, state, and transit fleets, private truck companies, ferries, tourist boats and launches, locomotives, power generators, home heating furnaces, and other equipment, especially in the agricultural sector. Regulated fleets are being rewarded for implementing biodiesel use into their heavy-duty vehicles. For every 1700 litres of biodiesel used in any blend level per year, a provision under the Energy Policy Act of 1992, as amended in 1998, credits these fleets with one required alternative-fuel light-duty vehicle. Furthermore, there is growing interest in using biodiesel where workers and school children are exposed to toxic diesel exhaust, in aircraft to control local pollution near airports, and in locomotives and power generators that face restricted use unless emissions can be reduced. One example is Eastman Chemical Co. of Kingsport, Tennessee, who have switched all 200 delivery vehicles over to biodiesel B20 use.

1.2 Research Objectives

The main objective for this research is to produce biodiesel from rubber seed oil by two step method and to study the properties of biodiesel produced.

1.3 Scope of Study

In order to achieve the objective, there are several scope was have been identified

1. Extraction of RSO by two different methods, such as Sohxlet and microwave extraction.
2. Characterization of the RSO

3. Synthesis of biodiesel from the oil by two-step method.

1.4 Problem Statement

Rubber seed oil is one of the non edible oil but still the use of rubber seed oil in industry is not so efficient compared to other feedstocks. Rubber seed oil contains a high significant percentage of free fatty acid.

An experiment should be conducted to see whether rubber seed oil can be used as an oil to produce biodiesel or not. The viscosity of rubber seed oil is high. Hence, a comparison should be made to see whether the biodiesel produced from rubber seed oil still contains high viscosity or not.

Different origin has different value of oil content in rubber seed. Hence, we do not know which origin has the optimum oil content. The source of rubber seed from Malaysia has taken to analysis the oil content.

Direct transesterification is not feasible in rubber seed oil because rubber seed oil contains high percentage of FFA. High percentage of FFA leads to the formation of soap in the oil. Hence, a best method should be studied for producing biodiesel from rubber seed oil.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

Biodiesel is produced from the vegetable oil or animal fats. It is either produced from edible oil or non edible oil. But in the present time, production of biodiesel from non edible oil is feasible because it's safe and less pollute to the environment.

Biodiesel is environmentally friendly compared to petrol diesel. It reduces the emission of carbon monoxide and carbon dioxide. Biodiesel also contains high cetane rating compared to petrol diesel[1]. Hence, it can improve the performance of the engine.

Biodiesel is produced by using vegetable oils and animal fats. The main components of vegetable oils and animal fats are triglycerides or also known as esters of fatty acids attached to a glycerol. The triglycerides contain several different fatty acids. These fatty acids differ from each other by their physical and chemical composition. Hence, these fatty acids will be the parameter in influencing the property of the vegetable oil and animal fat. This oil contains high viscosity and that is the main obstangle to use it as a fuel. Chemical reactions are used to lower the viscosity of these oils.

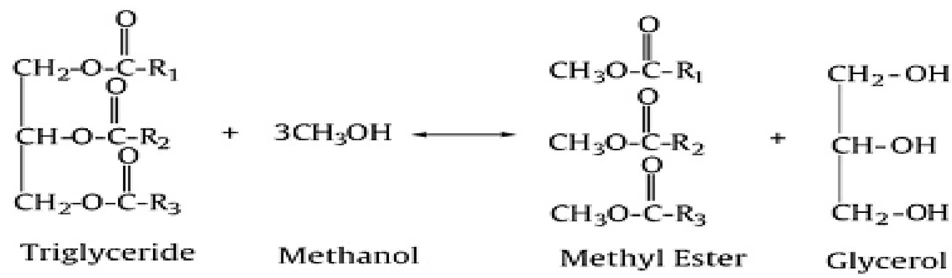

Figure 2.1: Esterification of TG

In that reaction, triglycerides are converted into fatty acid methylester (FAME), in the presence of short chain alcohol, such asmethanol orethanol, and a catalyst, such as alkali or acid, with glycerol as a by-product.

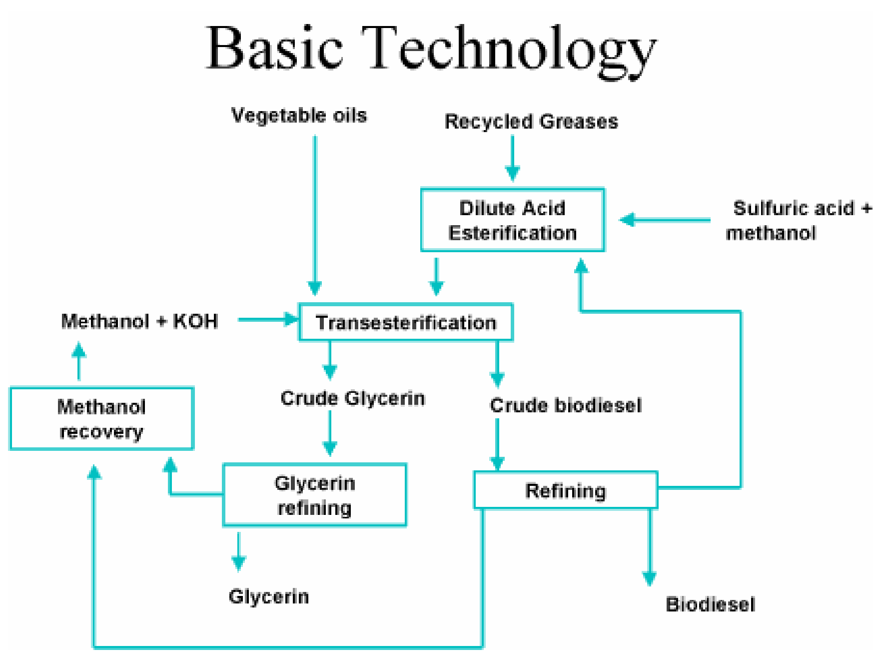

Figure 2.2: Transesterification process route

The transesterification process reacts an alcohol (like methanol) with the triglyceride oils contained in vegetable oils, animal fats forming fatty acid alkyl esters (biodiesel) and glycerin. The reaction requires heat and a strong base catalyst, such as sodium hydroxide or potassium hydroxide. The simplified transesterification reaction is shown below.

Triglycerides + Free Fatty Acids (<4%) + Alcohol $\xrightarrow{\text{Base}}$ Alkyl esters + glycerin

Figure 2.3: Transesterification process

Feedstocks with more than 4% free fatty acids, which include inedible animal fats and recycled greases, must be pretreated in an acid esterification process. In this step, the feedstock is reacted with an alcohol (like methanol) in the presence of a strong acid catalyst , converting the free fatty acids into biodiesel. The remaining triglycerides are converted to biodiesel in the transesterification reaction.

Triglycerides + Free Fatty Acids (>4%) + Alcohol $\xrightarrow{\text{Acid}}$ Alkyl esters + triglycerides

Figure 2.4: Acid esterification catalysed reaction